DETERMINATION OF THE PARAMETERS OF THE EQUATION OF STATE OF A LIQUID BY PLANNED THERMOPHYSICAL EXPERIMENT

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The problem of planning liquid-phase measurements to determine the constants of the equation of state is solved.

The design and development of modern energy production equipment and chemicotechnological processes is impossible without a knowledge of the thermodynamic properties of the reagents and heat transport fluids involved. The most complete and exact information on these quantities is usually obtained from thermophysical P—v—T experiments and subsequent construction of an equation of state. However, carrying out wide-range experimental studies requires significant expenditures of material and time.

Thus, it would be of major significance to develop methods for planning experiments which would achieve the desired goal most efficiently [1].

In the present study we will consider the problem of planning P—v—T measurements in the liquid phase of a pure substance in order to determine the unknown coefficients of the equation of state. The quality of the solution to this problem depends to a great degree on the choice of mathematical model, i.e., the equation of state. For the latter we will use

$$z = 1 - 1.744\frac{\varepsilon_1}{kT}[(b_{01}\rho)^2 - 0.4654\,(b_{01}\rho)^4], \tag{1}$$

which was obtained in [2] using a cellular model of the liquid in combination with the (12, 6) effective potential with temperature-dependent potential parameters. It is valid for the temperature range $T_{tr} \leq T \leq T_c$ and $\rho \geq 1.8\rho_c$. Equation (1) is theoretically sound and describes the thermal properties of single-phase liquids with high accuracy ($\delta\rho$ = 0.01-0.2%). This fact has been tested for a large number of materials, including polar and nonpolar liquids. We note that, in accordance with (3), the parameters of equation of state (1) ε_1 and b_{01} can be represented analytically:

$$\frac{\varepsilon_1}{k} = 0.795T_c \exp(c(1 - T/T_c)],$$

$$\sigma_1^{-3} = a - bT,\ b_{01} = 2\pi N\sigma_1^3/3. \tag{2}$$

Thus, equation of state (1) contains only three constants, *a*, b, and c, which must be determined from the minimum number of experimental points. This opens possibilities for designing experiments.

Using the method of planning thermophysical experiments developed in [4], one can reduce the required number of experimental points to the number of unknown coefficients in Eq. (1).

The problem of creating an optimum plan consists of finding a disposition of experimental points in the planning space which will satisfy the corresponding optimality criterion [1].

In the present study we will use the D-optimality criterion to design the experiment. The plan, i.e., the set of points at which it is necessary to perform measurements, is D-optimal if the determinant of its covariation matrix is minimal, and the determinant of the corresponding Fisher information matrix is maximal [1].

The numerical procedure for finding the optimum plan consists of using the direct method for search for the maximum of the Fisher information matrix [5].

Given the nonlinear dependence of Eq. (1) on the parameters *a*, b, and c, construction of the plan is complicated by the fact that the elements of the minimizing functional depend on

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TABLE 1. D-Optimal Experimental Plan for Determination of Constants of Eq. (1) for Ethane

Point number	τ	ω	T, K	ρ, kg/m³
1	0,872	2,54	266,4	517,8
2	0,436	2,99	133,1	611,3
3	0,329	3,25	100,7	662,4

TABLE 2. Histogram of Deviations of Experimental Values of Ethane Density [6] from Calculations

Deviation interval $\delta\rho$, %	No. of exptl. points	Deviation interval $\delta\rho$, %	No. of exptl. points
$0,3\geqslant\delta\geqslant0,2$	0	$-0,1>\delta\geqslant-0,2$	10
$0,2>\delta\geqslant0,1$	1	$-0,2>\delta\geqslant-0,3$	6
$0,1>\delta\geqslant0,0$	36	$-0,3>\delta\geqslant-0,4$	4
$0,0>\delta\geqslant-0,1$	40		

the true values of the constants being found. Therefore, before developing a plan for the nonlinear model, it is necessary to linearize it relative to the unknown constants and provide initial estimates.

Using the example of ethane, below we will consider an optimum plan for performing P–v–T measurements in the liquid phase to determine the constants of equation of state (1). The plan was developed for the temperature range $100 \leq T \leq 270$°K and reduced densities of $2.0 \leq \omega \leq 3.3$ ($\rho_c = 204$ kg/m^3). The numerical values $a = 0.03$, $b = 0.005$, $c = 2.18$, previously determined for methane, were used as initial estimates.

The D-optimal plan for performing P–v–T measurements is presented in Table 1. Three experimental points from [6], closest to the points of the plan, were used to determine a, b, and c of Eq. (1). Their values proved equal to $a = 0.02127$, $b = 0.00270$, $c = 2.57$.

It is of interest to test the reliability of equation of state (1) with the three constants thus found. To do this, values of liquid ethane density calculated with Eq. (1) were compared with the experimental data of [6]. The data of [6] encompass pressure and temperature ranges of P = 1.2-60 MPa and T = 90-270°K. A clear picture of the agreement between calculation and experiment is given by Table 2, which characterizes the histogram of deviations of experimental density values (96 points) from calculated ones. As is evident from the table, the great majority of experimental data is described with an error $\delta\rho = 0$-0.2%, and only at four points does it rise to $\delta\rho = 0.3$-0.4%. Such a description of experiment can be considered satisfactory.

Analysis of the results obtained shows that for a suitable choice of the equation of state the method of experiment planning can significantly reduce the volume of experimental studies required without loss of accuracy in the equation of state.

NOTATION

$z = Pv/Rt$; P, pressure; v, volume; T, temperature; ρ, density; T_c, ρ_c, critical parameters; T_{tr}, triple point temperature; $\omega = \rho/\rho_c$; k, Boltzmann's constant; N, Avogadro's number.

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THREE-REFERENCE-CURVE METHOD IN CONSTRUCTING THE EQUATION OF STATE OF A GAS AND A LIQUID

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A method of constructing the thermal equation of state of a gas and a liquid is considered; the method requires information only on three reference curves.

In [1-4], methods of constructing an equation of state common to gas and liquid were proposed on the basis of the use of a well-known thermodynamic relation between the thermal parameters of the material and its internal energy. The fundamental feature of these methods is the use of reference curves chosen on the thermal surface of the material and satisfying definite requirements in constructing the equation of state.

In developing the equation of state within the framework of the above-noted methods, two different approaches may be distinguished: in one, only one reference curve is used [1]; in the other, two basic curves are used [2-4]. The second approach offers great possibilities. On the one hand, it allows a complex multiconstant equation describing both thermal and caloric properties of the material with near-experimental accuracy to be constructed [2]. On the other, the use of two reference curves offers the possibility of developing an equation of state of gas and liquid of relatively simple form, requiring a minimum of a priori experimental information, suitable for use in solving a wide range of practical problems [3, 4]. Equations of this class are called engineering equations of state. For example, in [4], the simplest version of a unified equation of state for gas and liquid obtained on the basis of two reference curves — the ideal-gas curve $T_{IG}(\rho)$ and the saturation line $T_S(\rho)$ — was considered:

$$p(\rho, T) = \frac{RT}{\mu}\rho - \left[\frac{RT_S(\rho)}{\mu}\rho - p_S(T_S)\right]\frac{T_{IG}(\rho) - T}{T_{IG}(\rho) - T_S(\rho)}, \qquad (1)$$

where $p_S(T_S)$ is the equation of saturated vapor pressure.

Note that the term "ideal-gas curve" used here and in many other works is not entirely appropriate. Below, the curve of the thermodynamic surface of the material characterized by a single compressibility will be called the Bachinskii curve and denoted by $T_Z(\rho)$; Bachinskii [5] was one of the first researchers to study the features of this curve.

Qualitative analysis of Eq. (1) confirms its advantages resulting from the choice of the liquid—vapor equilibrium line and the Bachinskii curve as the reference curves. It rigorously gives two universal reference curves, is defined over a broad density range from zero to the liquid density at the triple point, satisfies the critical conditions and, in the limiting case as $\rho \to 0$, ensures transition to the ideal-gas equation. In addition, Eq. (1) is distinguished by simplicity of structure, requires a limited quantity of experimental data in its construction, and may be used for a series of thermodynamically similar materials.

Quantitative analysis of Eq. (1) for argon, using a dependence approximating the saturation and extensibility lines [4], shows that the mean-square deviation of the thermal parameters calculated using Eq. (1) from the reference data is 1.3% with respect to the density, for the whole mass of reference experimental data [6-10]. Taking account of the structural

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